

An alternative removal strategy for perfluorooctane sulfonate from aqueous film-forming foam solution by aeration-foam collection

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Introduction

Aqueous film-forming foams (AFFFs) used in fire-fighting are one of the main contamination sources of perfluorooctane sulfonate (PFOS) to the subterranean environment, requiring high costs for remediation¹. In this study, a method that combined aeration and foam collection was presented to remove PFOS from a commercially available AFFF solution². The method utilized the strong surfactant properties of PFOS that cause it to be highly enriched at air-water interfaces. Aeration-foam collection was found to be effective for the removal of high concentrations of PFOS from AFFF-contaminated wastewater, and the concentrated PFOS in the collected foam can be reused.

Materials and methods

PFOS, perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS), and perfluorooctanoate (PFOA) (all purity > 98%) were purchased from Sigma-Aldrich Co. Sodium p-perfluorooctane sulfonate (OBS, purity > 94%) was purchased from Shanghai 3F Corporation, China. N-Octyl- β -D-glucopyranoside (a kind of non-ionic surfactants, purity > 97%), commonly used in the AFFF industry, was purchased from Aladdin Industrial Co. An AFFF concentrate was kindly provided by Jiangsu Suolong Fire Science and Technology Co., Ltd., China, whose major compositions were PFOS (around 3 g/L), diethylene glycol butyl ether (DGBE, around 180 g/L) and APGs (around 50 g/L). A cylindrical aeration device was displayed in Fig. 1, and a titanium air diffuser with a pore diameter of 10 μ m was placed at the bottom. Foams formed during aeration were evacuated through the foam valves on the upper half of the device. The collected foams were transmitted through a tube and settled in a tank overnight to allow the foam to break up. All the aeration experiments were conducted with 600 mL of PFOS solution. The initial PFOS concentration, pH value of the solution and aeration flow rate were adjusted to evaluate the efficiency of aeration-foam collection under different circumstance.

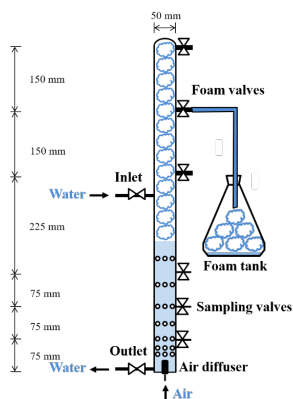


Fig. 1. Setup for PFOS removal by aeration-foam collection.

Results and discussion:

As showed in Fig. 2, PFOS elimination rates increased significantly with increasing aeration flow rates. At the aeration flow rates of 100 mL/min and 125 mL/min, PFOS removal percent reached 99% within 100 min and 50 min, respectively. Increasing the aeration flow rates caused an increase in the foam volume, and thus decreased the corresponding PFOS concentrations in the foams (C_{foam}). At an aeration rate of 75 mL/min, the PFOS elimination rate was comparatively fast and the C_{foam} was 6.50 mmol/L, much higher than the corresponding concentration (1.70 mmol/L) with an aeration flow rate of 100 mL/min. Therefore, an aeration rate of 75 mL/min was chosen to conduct all the following experiments described below.

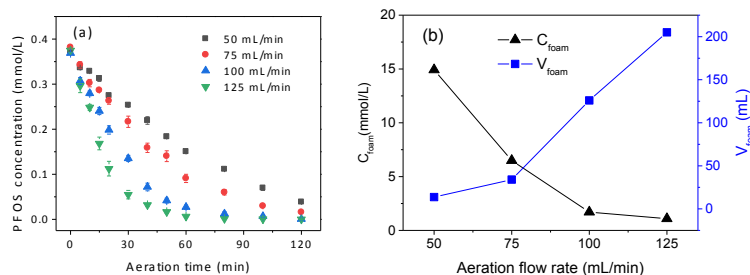


Fig. 2. Effect of aeration flow rates on PFOS concentrations in solution at different time (a), the volume and concentration of the foam (b) collected after 2 h.

Fig. 3 showed the influence of initial PFOS concentration (C_{initial}) on the removal efficiency. The removal efficiency of PFOS decreased with the increase of C_{initial} from 0.093 mmol/L to 0.382 mmol/L. A high concentration of PFOS in the foam was preferable for the stability of air bubbles, preventing foams from breaking and increasing foam volume. Consequently, the enrichment of PFOS in the foams would be decreased as well as the PFOS removal percents. On the whole, aeration was effective for the removal of PFOS from wastewater within a wide range of PFOS concentrations, widening the practical application of aeration and foam collection.

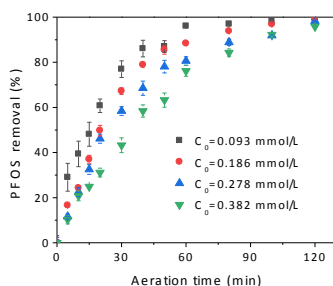


Fig. 3. Effect of initial PFOS concentrations on PFOS removal percents by aeration-foam collection.

The influence of the ionic strength on PFOS elimination was displayed in Fig. 4a. The PFOS elimination rates increased and then remained stable with increasing NaCl concentrations. Overall, high ionic strength was beneficial for the removal of PFOS by aeration-foam collection. Firstly, the effect of ionic strength might be explained by the reduction in solubility of PFOS in water with increasing NaCl concentrations, making it more preferable for the PFOS to adsorb on the surface of air bubbles³. Secondly, the diameter of air bubbles would be smaller at higher ionic strength. The addition of electrolytes could lower the hydrophobic attractive force between approaching bubbles and inhibit the bubble coalescence and decrease their size, resulting in an increase in the total available surface area for adsorption at the air-water interface⁴.

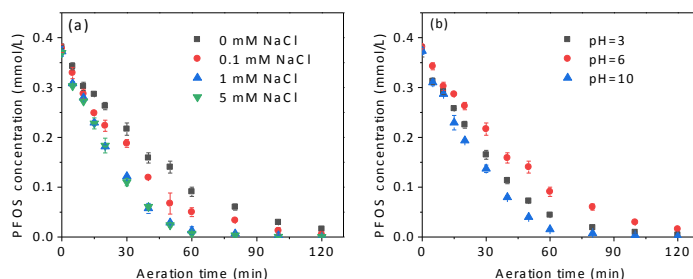


Fig. 4. Influence of ionic strength (a) and pH (b) on PFOS elimination by aeration-foam collection.

Fig. 4b showed the influence of solution pH on PFOS removal by aeration. Both acidic and basic solutions were

more favorable for PFOS removal by aeration than the neutral solution. As discussed in the influence of the ionic strength, both the acidic and basic solutions had higher ionic strength than the neutral solution, making aeration more effective. Among them, the acidic solution was less effective than basic solution since the excessive hydrogen ions in the acid solution may neutralize the negative charges on air bubbles and decrease their stability.

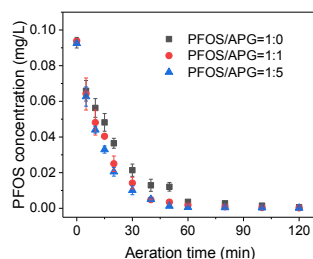


Fig. 5. Influence of co-existed APG on PFOS elimination by aeration-foam collection.

Apart from fluorinated surfactants, AFFFs contain even higher concentrations of hydrocarbon surfactants, such as alkyl polyglycosides (APGs). In this study, N-Octyl- β -D-glucopyranoside was chosen to represent the typical APG components. The influence of co-existing APG on the removal of PFOS by aeration was illustrated in Fig. 5. APGs increased the total amount of surfactants in solution, which helped to stabilize the air bubbles and thus assisted PFOS removal through increased foam formation. In the meantime, APG could be partially removed with PFOS as a non-ionic surfactant. After aeration for 2 h, the total organic carbon (TOC) of the solution (PFOS/APG=1/1) dropped from 17.7 mg/L to 5.4 mg/L, suggesting APG was removed together with PFOS. However, without the presence of PFOS, the surface activity of APG was not enough to form stable foams on the surface independently and no APG was removed. This result implied that the presence of APG in AFFF-contaminated wastewater was beneficial for PFOS removal by aeration-foam collection. On the contrary, APG usually hindered the treatment of AFFF-contaminated wastewaters by other methods, such as adsorption, due to the competitive adsorption and poor selectivity of adsorbents⁵.

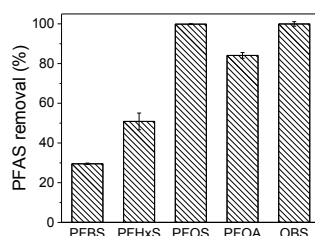


Fig. 6. Removal of different PFCs by aeration-foam collection

Considering new substitutes of PFOS used in the AFFF industry as well as the wide range of other PFAS contamination problems, it's important to know whether this method is effective for other PFASs. OBS and some short-chain PFASs are the most common substitutes for PFOS in AFFF products. The results for different PFAS removal after aeration for 2 h with the assistance of APG are displayed in Fig. 6, and it can be seen that aeration was more efficient for long-chain PFASs like PFOS and OBS, and less efficient for PFBS, PFHxS and PFOA. The short-chain PFASs like PFBS and PFHxS are more soluble in water and less surface active and thus they are more weakly adsorbed at the air-water interface than PFOS. Although less efficient than for PFOS, aeration-foam collection of short-chain PFASs may still be attractive given that there are currently few options for the removal of short-chain PFASs from contaminated waters. In comparison with other traditional treatments, such as adsorption, aeration-foam collection is of great potential by removing over 50% PFHxS and 30% of PFBS by aeration for only 2 h. The key issue for aeration was to form enough foam and collect foams from the upper half of the device. In future experiments conducted for the short-chain PFASs, it would be useful to determine if the addition of more APG to the solution can accelerate the formation of foam, and also if decreasing the foam depth by using a lower foam valve can improve foam collection.

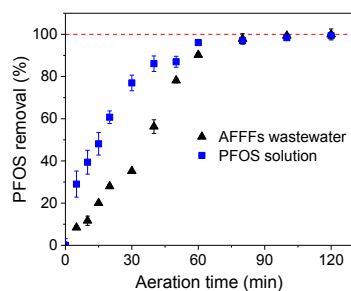


Fig. 7. Comparative PFOS removal from AFFF solution and PFOS solution by aeration-foam collection.

To evaluate the application of aeration-foam collection for real wastewater, AFFF solution was prepared by diluting the AFFF stock solution to conduct aeration experiments. As shown in Fig. 7, the PFOS removal percents in AFFF solutions were lower than those in the PFOS solutions. The concentration of PFOS in the AFFF was as high as 3 g/L, much higher than its solubility in water. The increased solubility of PFOS in the AFFF solution made it less preferable to be accumulated on the surface of air bubbles. However, the elimination of PFOS by aeration and foam collection was over 99.3% after aeration for 100 min, which was quite efficient compared to other treatments. Evidently, aeration-foam collection could be used as a promising technology for the removal of PFOS from real AFFF-contaminated wastewaters.

Aeration-foam collection is demonstrated to be effective for PFOS removal from AFFF-contaminated wastewater in this study. Increasing the aeration flow rate, ionic strength and co-existing surfactant, as well as decreasing the initial PFOS concentration increased the removal percent of PFOS, but decreased the enrichment of PFOS in the foams. For wastewater containing high concentrations of PFOS, collection of the foams on the solution surface during aeration may facilitate the recovery and reuse of PFOS and thus reduce further contamination of the subsurface environment. After aeration treatment, PFOS concentrations in the residual solution decreased to $\mu\text{g/L}$ levels, and adsorption by activated carbon or resins may be used to further remove the low concentrations of PFOS. In addition, aeration-aerosol collection could also be considered, in which aerosols formed continuously during aeration at the surface of the water solution would be collected and the concentrated aerosol waste disposed of using a suitable technology.

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